Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wildfire, and ecological implications

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A R T I C L E   I N F O

Article history:
Received 13 January 2010
Received in revised form 28 April 2010
Accepted 30 April 2010

Keywords:
Phosphorus
Atmospheric deposition
Forest fire
Eutrophication
Sierra Nevada

A B S T R A C T

The dry deposition of atmospheric particulate matter can be a significant source of phosphorus (P) to oligotrophic aquatic ecosystems, including high-elevation lakes. In this study, measurements of the mass concentration and size distribution of aerosol particles and associated particulate P are reported for the southern Sierra Nevada, California, for the period July–October, 2008. Coarse and fine particle samples were collected with Stacked Filter Units and analyzed for Total P (TP) and inorganic P (IP) using a digestion-extraction procedure, with organic P (OP) calculated by difference. Particle size-resolved mass and TP distributions were determined concurrently using a MOUDI cascade impactor. Aerosol mass concentrations were significantly elevated at the study site, primarily due to transport from distant sources and emissions from local and regional wildfires. Atmospheric TP concentrations ranged from 11 to 75 ng m −3 (mean = 37 ± 16 ng m −3), and were typically dominated by IP. Phosphorus was concentrated in the coarse (>1 μm diameter) particle fraction and was particularly enriched in the 1.0–3.2 μm size range, which accounted for 30–60% of the atmospheric TP load. Wildfire emissions varied widely in P content, and may be related to fire intensity. The estimated dry depositional flux of TP for each daily sampling period ranged between 7 and 118 μg m −2 d −1, with a mean value of 40 ± 27 μg m −2 d −1. Relative rates of dry deposition of N and P in the Sierra Nevada are consistent with increasing incidence of N limitation of phytoplankton growth and previously observed long-term eutrophication of lakes.

1. Introduction

Unlike carbon and nitrogen, phosphorus (P) has no significant gaseous phase under standard temperature and pressure conditions and is therefore almost entirely particle-associated in the atmosphere. Consequently, atmospheric inputs of P to ecosystems have traditionally been thought to be negligible in comparison with other sources and have not typically been included in P cycling studies (Graham and Duce, 1979). However, the ecological importance of particulate P deposition is accentuated in ecosystems where sources of P are otherwise low. For example, in the oligotrophic surface waters of the Mediterranean Sea, atmospheric P inputs have been observed to sustain primary production during seasonal periods of maximum stratification (Herut et al., 2002; Markaki et al., 2003; Migon et al., 2001). There is also evidence that some highly productive tropical forest and savannah ecosystems are reliant upon the input of atmospheric P from distant regions to maintain primary production over the long term (Okin et al., 2004).

Atmospheric transport has the potential to significantly impact nutrient cycling in montane and high-elevation ecosystems of the Sierra Nevada, California, as these systems are particularly sensitive to the effects of atmospheric deposition due to the low nutrient content of their predominantly granitic parent materials (Melack and Stoddard, 1991). The eutrophication of Sierra Nevada lakes due to the atmospheric input of nutrients has been noted in several studies, the majority of the ecosystem effects having been attributed to nitrogen deposition (Jassby et al., 1994; Schuster and Grismer, 2004). However, there is some evidence that atmospheric inputs of P may also be driving long-term ecological changes in lakes of this region (Jassby et al., 1994; Zhang et al., 2002). In a 18-year study of Emerald Lake, Sickman et al. (2003) observed a two- to three-fold increase in algal biomass and a shift from P limitation toward more frequent N limitation of phytoplankton abundance. These trends were reflected in a larger set of Sierra Nevada lakes sampled as part of synoptic surveys between 1985 and 1999; nitrate decreased and total P increased in >70% of the lakes sampled. The authors hypothesized that the trends at Emerald Lake and the regional lake changes resulted from input of P from the atmosphere and proposed that the transport of atmospheric pollution from the
San Joaquin Valley could be contributing to the eutrophication of Sierra Nevada lakes. While P has been measured in wet deposition samples collected in the Sierra Nevada, very few measurements of P in atmospheric aerosols have been made in this region; as with nitrogen, dry deposition of P will likely equal or exceed wet deposition of P (Sickman et al., 2003). These findings provide a strong justification for an investigation into the biogeochemical role played by atmospheric P inputs in the trophic dynamics of high-elevation lakes of the Sierra Nevada.

The quantification of P in dry deposition samples collected in natural settings has proven to be problematic, often due to sample contamination issues, and several techniques have been applied with varying degrees of success (Ahn and James, 1999; Tsukuda et al., 2005). As an alternative to direct measurements, dry deposition of P can be quantified through the application of an estimated or modeled particle deposition velocity, which can be used in conjunction with concentration data to estimate atmospheric flux (Markaki et al., 2003). Because the deposition velocity of atmospheric particles is known to vary with aerodynamic diameter ($D_a$) (Holsen and Noll, 1992), information on the size distribution of particle-associated P must be obtained in order to accurately estimate deposition rates. While P has been observed to reside predominantly in the coarse particle mode (Chen et al., 2007; Mahowald et al., 2008), there is presently very little data on the particle size-resolved distribution of atmospheric P. This is a fundamental limitation to previous studies that have attempted to estimate P deposition by assuming a single deposition velocity or uniform P distribution across all particle size classes (Chen et al., 2007; Migon et al., 2001).

In this study, measurements of the mass concentrations and size distributions of atmospheric particulate matter (PM) and inorganic and organic P are reported for a site in the southern Sierra Nevada for the period July—October 2008. During this time of the year, air quality is significantly degraded in the southern Sierra Nevada due to the transport of air pollutants by predominantly westerly winds. Dry deposition was expected to represent a majority of the atmospheric flux during this period due to relatively low amounts of dry-season precipitation and high particle loading from human activities in the adjacent San Joaquin Valley. Particle size-resolved distributions were used to generate estimates of P dry deposition using a size-weighted deposition velocity model. These estimates of P deposition are then compared to known pools and fluxes in the Emerald Lake watershed to assess their significance to the P biogeochemistry of high-elevation lakes of the Sierra Nevada.

2. Materials and methods

2.1. Aerosol sampling

Sampling was conducted at the Lower Kaweah monitoring station (36°33’58”N, 118°46’40”W; 1905 m above sea level, Fig. 1), located in Sequoia National Park, in the southern Sierra Nevada, California. The Lower Kaweah station is situated on a west-facing rocky outcrop in a mixed conifer forest, about 1500 m from the nearest major road, and is therefore relatively sheltered from local sources of aerosol particles. The site is an air quality monitoring station operated by the National Park Service Air Resources Division and has been the location of previous atmospheric studies (e.g., Bytnerowicz et al., 2002). In addition to the availability of historic data, the site is equipped with meteorological instruments which routinely measure air temperature, wind speed and direction, and relative humidity.

Atmospheric particulate matter (PM) samples were collected during the period July 1—October 27, 2008. Dichotomous sampling
was conducted using Stacked Filter Unit (SFU) samplers (Cahill et al., 1979), which collected coarse and fine PM samples integrated over 24 or 48 h, and were operated at a flow rate of 20 L min⁻¹. The SFUs use a multiple filter holder to fractionate aerosol samples, which are collected on 47 mm Whatman Nucleapore polycarbonate membrane filters. A 5 μm pore size filter captured coarse particles (1 μm < Dp < 15 μm), while fine PM (Dp < 1 μm) passed through and was deposited on a 0.4 μm polycarbonate membrane filter.

Particle size-resolved mass distributions were determined using a Micro-Orifice Uniform Deposit Impactor (MOUDI) sampler (Marple et al., 1991), which was installed inside of a climate-controlled instrument shelter. The MOUDI aerodynamically fractionated particles into 11 size classes with cuts at 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and 0.056 μm Dp. MOUDI samples were collected via impaction onto 47 mm polycarbonate membrane filters (0.2 μm), while a 37 mm after-filter collected ultrafine particles (<0.056 μm). The 47 mm membrane filters used in the MOUDI sampler were coated with a silicone spray prior to field deployment to minimize the effects of particle bounce (Chang et al., 1999). The MOUDI typically collected samples integrated over 7–10 days and was operated at an average flow rate of 30 L min⁻¹. This deployment interval was necessary in order to collect enough atmospheric PM for P analysis.

Field blanks for SFU filters and MOUDI impaction substrates were collected at regular intervals and were subjected to all of the same storage, handling, and analytical procedures as field samples. After sampling, all filters were folded and placed into clean Petri dishes. Samples were then stored in a freezer at −20 °C before further analysis. Particle mass concentrations were determined via gravimetric analysis, whereby MOUDI and SFU filters were weighed before and after field deployment using a Sartorius ME-5 microbalance with 1 μg readability and 5 μg repeatability. Prior to weighing, filters were stored for at least 48 h under controlled relative humidity (50%) and temperature (20 °C) conditions to minimize variations in filter mass caused by differences in moisture content. Variations in mass caused by electrostatic charges were controlled using a 210Po alpha particle source (Truzzi et al., 2005). The method detection limit for particle mass was estimated to be three times the standard deviation of laboratory blanks and was approximately 20 μg, corresponding to atmospheric concentrations of about 1 and 0.1 μg m⁻³ for SFU and MOUDI samples, respectively.

2.2. Atmospheric P analysis

Total P (TP) and total inorganic P (IP) were determined for all SFU samples using a digestion procedure adapted from Chen et al. (2006). Coarse and fine PM filter samples from each sampling period were split into two equal subsamples. The first subsample, which is designated in this study as TP, was combusted in a closed container overnight at 550 °C and then extracted via sonication for 12 h with 10 ml of 1 N HCl. The second subsample was extracted with 10 ml of 1 N HCl without ashing, and is designated as inorganic P (IP). Organic P (OP) was estimated by subtracting IP from TP for each SFU sampling period, providing a minimum measure of OP. Due to the small sample size, MOUDI filters were not split into subsamples for TP and IP determination, but were analyzed only for TP using the combustion and extraction procedure described above. IP content for all samples was determined on neutralized digestion extracts via the “molybdenum blue” method (Murphy and Riley, 1962), using a Varian Cary 50 spectrophotometer with a 5 cm quartz cell. The method detection limit obtained for TP (defined as the standard deviation of field blanks times three) was approximately 0.06 μmol L⁻¹ for all filter types (approximately 1 and 0.1 ng m⁻³) for SFU and MOUDI samples, respectively. TP values for blanks (i.e., blank filter and reagents) were consistently below the method detection limit. There is presently no certified atmospheric PM reference material available for P; therefore, the accuracy of the TP analysis procedure used in this study was checked against a marine sediment reference material (SRM 2702, Inorganics in Marine Sediment) provided by the National Institute of Standards and Technology. SRM 2702 was included in all analytical runs and recoveries averaged 98 ± 5% (n = 33).

3. Results

3.1. General characteristics of atmospheric TP, PM loading, and air masses

Atmospheric TP concentrations during the study ranged from 11 to 75 ng m⁻³ (mean = 37 ± 16 ng m⁻³), as shown in Fig. 2. Such values are nearly an order of magnitude higher than those observed in other locations in the Sierra Nevada (Mahowald et al., 2008), although they are similar to measurements made in the heavily urbanized Lake Tahoe basin (Zhang et al., 2002). TP maxima generally coincided with peaks in coarse PM concentration and the correlation between the two variables was statistically significant (r² = 0.83, p < 0.001), suggesting that TP dynamics at Lower Kaweah are driven primarily by variability in the atmospheric burden of particles with aerodynamic diameters >1 μm, an observation in agreement with previous studies (Mahowald et al., 2008).

Total PM concentrations (Dp < 15 μm) measured in this study ranged between 8 and 105 μg m⁻³ (Fig. 2), with a mean value and standard deviation of 22 ± 16 μg m⁻³. Maximum particulate loads were observed during the period September 16–23 and were caused by emissions from a local wildfire named the “Hidden Fire”, which occurred approximately 5 km from the sampling site (Fig. 1). Wildfire emissions led to especially high fine PM concentrations (85 μg m⁻³), although coarse PM also peaked during this time, most likely due to the entrainment of soil particles during the fire (Mahowald et al., 2005). Interestingly, the PM maxima observed during the Hidden Fire did not result in high TP concentrations, suggesting that local wildfires were not an important source of P to the atmosphere in the surrounding area. Additional maxima for fine PM occurred in early July and were concurrent with multiple forest fires in northern and central California that had led to widespread smoky conditions in the southern Sierra Nevada at the time (Wegesser et al., 2009). Fine and coarse PM concentrations both fell to ~50% of their mean values during the month of October, with the lowest loads being observed just after a small (~8 mm) precipitation event that occurred at the site during the period October 3–5.
The results of 3-day air mass back trajectory (AMBT, Fig. 3a–d) data indicate that air masses reaching the Lower Kaweah site most frequently arrived from a westerly or northwesterly direction (Fig. 3c), passing over the Pacific ocean, the San Francisco Bay area, and the San Joaquin Valley en route. These air masses typically transport large quantities of particles due to the buildup of particulate emissions in the San Joaquin Valley associated with “Fresno Eddy” recirculation events, and are the primary cause of impaired air quality and reduced visibility within Sequoia National Park (Carroll and Dixon, 2002). Small-scale interruptions in this general trend were caused by atmospheric transport from the north (Fig. 3a and b), which was found to occur episodically during the sampling period (e.g., July 8–15 and September 1–15). From mid to late October, sampled air masses most frequently arrived from an easterly direction (Fig. 3d), passing over the mountain and desert regions of the southwestern U.S. This seasonal change in air mass origin corresponds with minima for both coarse and fine PM mass and TP, suggesting that atmospheric aerosol and P transport to the Lower Kaweah site is associated primarily with transport from west to east.

The mean daily temperature, relative humidity, and wind speed during the study period were 16.8 ± 4.3 °C, 45 ± 15%, and 1.7 ± 0.2 m s⁻¹, respectively. Relationships among these...
meteorological variables and PM mass were not statistically significant \((p > 0.05)\), suggesting that aerosol loading at the site is determined primarily by transport from offsite and is relatively insensitive to local conditions. There were no significant precipitation events during the study, with the exception of a small (8 mm) snow event in early October; therefore, dryfall can be assumed to account for the vast majority of atmospheric deposition during this period.

3.2. Size distribution and chemical speciation of atmospheric P

Temporal variations in coarse and fine TP mass concentrations are presented in Fig. 4, while particle size-resolved mass and TP distributions are shown in Fig. 5a–h. Particle concentration distributions are described as a function of particle size using log-scale diagrams:

\[ y = \frac{dC}{C_{\text{total}}} \log D_a, \]

where: \(C\) is the mass concentration of PM or TP for a given size stage, \(C_{\text{total}}\) is the total mass concentration of PM or TP for all size stages, and \(D_a\) values are the cut-points that characterize the range of particle sizes collected on each of the 11 impactor stages (Hinds, 1998). In Fig. 5, the mass-fraction associated with each impactor stage is equivalent to the area under the portion of the curve defined by the respective stage cut-points.

Fifty-two SFU sample sets (1 filter each for coarse and fine PM) were collected from July 2 to October 27 and analyzed for both TP and IP, with OP calculated by difference. Results of these measurements are summarized in Table 1 for the same time periods used for the MOUDI size distribution data, along with mean wind speed and the predominant AMBT trends during the sampling period. TP was above the detection limit (\(\sim 1\) ng m\(^{-3}\)) for every sample; however, the difference between TP and IP measurements was often very small, and in cases where it was less than twice the MDL for IP, OP was reported as below detection limit.

3.3. Dry deposition rate of atmospheric P

The dry depositional flux \(F_d\) of P on an aerial basis is given by the product of concentration \(C_d\) and deposition velocity \(V_d\) (Markaki et al., 2003):

\[ F_d = V_d \times C_d \]
The term $V_d$ is sensitive to particle size distribution and local meteorological conditions, and is thus very difficult to determine for atmospheric aerosols in natural settings (Holsen and Noll, 1992); therefore, P flux is typically calculated using $V_d$ values found in the literature. Duce and Tindale (1991) recommended $V_d$ values of 2 and 0.1 cm s$^{-1}$ for coarse (>1 μm) and submicron particles, respectively, and these estimates are generally in agreement with modeling and experimental studies (Noll et al., 2001); however, the use of only one of these estimates may lead to errors of two or three times the flux estimate when applied to P measurements derived from aerosol samples that are not size segregated (Herut et al., 2002). Deposition velocities have been found to be relatively similar for particles smaller than 1 μm under normal atmospheric conditions, while they can vary widely for coarse particles (Holsen and Noll, 1992), which often comprise the majority of the total atmospheric P flux. Therefore, we adopted a $V_d$ value of 0.1 cm s$^{-1}$ for inorganic and organic P in the submicron fraction (fine SFU sample), and a $V_d$ for coarse P was calculated for each sampling period by employing a mass-fraction weighting procedure using the TP size distribution data obtained from the MOUDI. $V_d$ estimates of 7.5, 5.2, and 0.5 cm s$^{-1}$ were assigned to the MOUDI stages 10–18, 5.6–10, 3.2–5.6, 1.8–3.2, and 1.0–1.8 μm, respectively, following Noll et al. (2001). The weighted $V_d$ estimated for coarse particle P was typically on the order of 1.5–2.0 cm s$^{-1}$ throughout the study period, similar to the 2.0 cm s$^{-1}$ value proposed by Duce and Tindale (1991). Maximum P deposition velocities (2.0–3.5 cm s$^{-1}$), which were estimated for early August, were higher than those typically reported in the literature, but are in the same range of estimates provided in Markaki et al. (2003).

Calculated TP dry deposition rates ranged from 7 to 118 μg m$^{-2}$ d$^{-1}$, with a mean value of 40 ± 27 μg m$^{-2}$ d$^{-1}$. Such values are similar to direct P deposition measurements made in high-elevation areas of the northern Sierra Nevada (Jassby et al., 1994) and the Mediterranean (Morales-Baquero et al., 2006), although they are somewhat higher than those predicted for the Sierra Nevada by atmospheric P deposition modeling (Mahowald et al., 2008). Coarse particles accounted for 92–99% of estimated P deposition throughout the study period. Most of this coarse TP flux was attributable to the deposition of IP (Fig. 6), which was concentrated in the coarse PM fraction throughout the study period. Maximum deposition rates occurred during the period August 9–12, when P was significantly enriched in the 10–18 μm size fraction, resulting in maximum estimated $V_d$ values.

### Table 1

<table>
<thead>
<tr>
<th>Period</th>
<th>Coarse mode</th>
<th>Fine mode</th>
<th>Mean wind speed m s$^{-1}$</th>
<th>Predominant atmospheric flow</th>
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<td></td>
<td>IP</td>
<td>OP</td>
<td>IP</td>
<td>OP</td>
</tr>
<tr>
<td>7/9–7/16</td>
<td>17.6</td>
<td>11.1</td>
<td>7.1</td>
<td>5.6</td>
</tr>
<tr>
<td>7/16–7/30</td>
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<td>3.1</td>
<td>4.6</td>
<td>2.3</td>
</tr>
<tr>
<td>7/30–8/13</td>
<td>27.4</td>
<td>8.5</td>
<td>5.5</td>
<td>4.3</td>
</tr>
<tr>
<td>8/13–8/28</td>
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<td>6.7</td>
<td>10.8</td>
<td>8.7</td>
</tr>
<tr>
<td>9/6–9/16</td>
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<td>6.2</td>
<td>8.7</td>
<td>2.0</td>
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<td>10.7</td>
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<td>6.5</td>
<td>6.2</td>
<td>BDL</td>
</tr>
<tr>
<td>10/10–10/27</td>
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<td>4.9</td>
<td>8.3</td>
<td>BDL</td>
</tr>
<tr>
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<td>7.2</td>
<td>7.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>9.4</td>
<td>7.6</td>
<td>3.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

*OP has been calculated for each sampling date as TP minus IP. The method detection limit is about 1.0 ng m$^{-2}$ for TP and IP. In cases where the difference between TP and IP is less than twice the method detection limit, OP has been reported as below detection limit (BDL).*

Fig. 6. Temporal variations in daily dry deposition flux for IP and OP.

### 4. Discussion

#### 4.1. Potential sources of atmospheric P

Atmospheric TP was consistently present at higher concentrations in the coarse PM fraction (mean = 26.7 ± 13.8 ng m$^{-2}$), with the coarse to fine PM ratio dropping below unity only on August 24. An examination of Fig. 5a–h reveals that particles in the 1.0–3.2 μm size range were particularly enriched in P, and this size class accounted for 30–60% of TP throughout the study period. Conversely, particles 1.0–3.2 μm in diameter rarely contributed as significantly to total PM mass, representing more than 40% of total PM only during the periods August 13–25 (Fig. 5d) and October 10–27 (Fig. 5h). The predominance of TP in 1.0–3.2 μm particles suggests that long-range transport, such as the transport of mineral aerosols from China, which has been observed to affect high-elevation sites of the Sierra Nevada (VanCuren and Cahill, 2002), could possibly be an important factor determining P loading at the site. This hypothesis is supported by detailed geochemical analysis and 11-day AMBT data reported by Vicars (2009). Particles larger than 3.2 μm, which have higher deposition velocities are thus more likely to originate from local or regional sources, seldom contributed a significant proportion of TP, representing more than 10% of TP only during the period July 30–August 13 (Fig. 5c). However, TP peaks in the coarse PM fraction were observed during this same period, indicating that particles >3.2 μm, while not normally present in relatively large amounts, have the ability to contribute to atmospheric P dynamics at the site.

PM mass had a bimodal size distribution throughout most of the study period, with the exception of July 1–9 (Fig. 2), and in September 16–23 (Fig. 5f), when the size distribution was dominated by particles <0.18 μm in diameter. Ultracfine particles were observed to account for more than 50% of total PM mass at these times, presumably due to the influence of forest fire emissions transported from northern California wildfires and the Hidden Fire, respectively (Fig. 1), which had caused smoky conditions during these periods. However, aerosol from the Hidden Fire was observed to have a very low TP concentration (less than 0.5 ng μg$^{-1}$ during both smoky periods). TP concentrations in particles <0.18 μm ranged from 0.7 to 1.4 ng μg$^{-1}$ during most other periods, with the exception of October 10–27, when values as high as 6.5 ng μg$^{-1}$ were observed. For most of the study period, submicron particulate P was enriched mainly in the 0.56–1.0 μm range, which accounted for 6–16% of TP for the duration of the study. Particles in this size range can consist of both primary aerosol and accumulation mode secondary aerosol, making it difficult to speculate as to the source of these P inputs. TP was detected at its highest fine PM concentrations during August 13–28 (Fig. 5d), concurrent with the total TP...
maxima (Fig. 2). Size distribution data indicates that this pulse of fine particulate P was attributable to high atmospheric TP concentrations not only in the 0.56–1.0 μm size range, but also in the <0.056 μm size range.

Coarse particle IP was consistently the most abundant atmospheric P species throughout the sampling period (mean = 18 ± 9 ng m⁻³), consistent with studies that suggest that mineral dust is globally the most important source of atmospheric P (Mahowald et al., 2008). The average coarse to fine particle IP ratio was 2.8 ± 1.7. Coarse particle IP rose to the highest concentrations during the second half of August, when values greater than 30 ng m⁻³ IP were detected in the coarse fraction for over a week (August 13–23). As shown in Fig. 5d, this IP resided in the 1–3.2 μm size range, which dominated the TP size distribution at the time.

Temporal variations in OP concentrations were offset for coarse and fine PM during most of the sampling period, and the correlation between OP in the two size fractions was not significant (p = 0.768) for sampling dates in which both were above the detection limit. Conversely, concentrations of coarse and fine particulate IP were significantly correlated (p = 0.045), suggesting that the sources of atmospheric IP are similar for both particle size classes, whereas sources of coarse and fine particulate OP are different. Maximum concentrations of both coarse and fine OP (49.3 and 18.9 ng m⁻³, respectively) occurred during the period July 10–13, when smoky atmospheric conditions prevailed throughout the southern Sierra Nevada due to the transport of wildfire emissions from northern California (Figs. 1 and 3a). This would seem to suggest that wildfire emissions are a significant source of OP; however, during the Hidden Fire (September 16–23, Fig. 5f), which caused far greater total PM mass concentrations at the study site than did the northern California fires, coarse and fine particulate OP increased only modestly, as did the total TP concentration.

4.2. Effects of local and regional wildfires

Our observations during the Hidden Fire seem to be in disagreement with Zhang et al. (2002) who reported P values of up to 800 ng m⁻³ for samples collected from an aircraft 35 km downwind of an intense forest fire plume in the northern Sierra Nevada. They assert that forest fire emissions were rich in OP, particularly in aerosol particles larger than 3.2 μm, (which contributed 40% of atmospheric P in the forest fire samples), but also due to contributions from an unidentified volatile organophosphorus compound, which accounted for over 20% of the total P. It is possible that our study underestimates atmospheric P concentrations during the Hidden Fire by neglecting to measure contributions from volatile P, such as phosphine, phosphides, and biogenic OP species. However, in some studies, plumes from biomass burning have been found to contain concentrations of P similar to background levels. For example, Echalar et al. (1995) performed an elemental characterization of aerosols from tropical forest and savannah fires and found that P was far more enriched in the savannah smoke plume relative to the tropical plume. They attributed this discrepancy to differing fire intensities and suggested that airborne P is produced to a much greater degree under flaming conditions, while the smoldering conditions typical of tropical forest fires are less conducive to P emissions. The central and northern California wildfires (Wegesser et al., 2009) were generally far more intense (i.e., flaming conditions) than the Hidden Fire and this may be a potential explanation for the conspicuously low atmospheric TP values measured during the Hidden Fire. Additionally, it has been suggested that forest fires tend to lead to emissions of P bound to very large aerosol particles (>100 μm) which do not travel far and are thus not measured at distant sampling stations (Mahowald et al., 2005).

4.3. Effects of atmospheric nutrient deposition on lakes

The rate of dry P deposition observed in this study is sufficiently high that atmospheric transport could be an ecologically significant source of P to high-elevation lakes of the southern Sierra Nevada, such as Emerald Lake (Tonnessen, 1991). In order to assess the potential ecological significance of dry P deposition to Emerald Lake, we applied the mean dry P deposition rate estimated in this study to the entire dry season (May–October) and compared the total atmospheric flux obtained to the other major annual P fluxes and P reservoirs within the watershed (Table 2). The majority of P in this study was observed to occur in association with aerosol particles less than 3.2 μm, suggesting a capacity for long-range transport. However, Emerald Lake is located at an elevation of 2800 m, approximately 800 m upslope from our sampling site, and it is unclear whether the particle concentrations and size distributions measured at the Lower Kaweah site can be applied directly to estimate dry deposition for the Emerald Lake watershed. Furthermore, the solubility of atmospheric TP is estimated to be only 32–36% (Baker et al., 2006), suggesting that a large proportion of the P input estimated in this study may not be readily available to aquatic organisms, although there is some evidence that insoluble atmospheric P may be at least partially bioavailable (Pulido-Villena et al., 2008). The flux estimate given in Table 2 should thus be considered an upper limit for biologically-active P in dry deposition to this watershed.

The estimated dry-season atmospheric P flux to the Emerald Lake watershed exceeds total (wet + dry) deposition estimates for the winter snowpack by 60%, in agreement with studies from the Mediterranean that have found annual P deposition to be mostly associated with dry deposition (Markaki et al., 2003; Morales-Baquero et al., 2006). Furthermore, dry-season P deposition enters the lake (either directly or via runoff caused by fall rain events) during the growing season, while P deposition during the winter is accumulated in the snowpack and enters the lake during snowmelt (April through June) when biological activity is very low. These observations are not inconsistent with the hypothesis that dry deposition is an important mechanism by which atmospheric P is delivered to phytoplankton in Emerald Lake. The annual total P deposition estimated in Table 2 exceeds the total catchment export, suggesting that atmospheric deposition is an important contributor to long-term P accumulation in the Emerald Lake watershed (Sickman et al., 2003).

It is reasonable to hypothesize that high-elevation ecosystems of the Sierra Nevada are dependant on exogenous nutrient sources. The concentration of P in Sierran granitoid rocks ranges from 0.06 to 0.08% by weight (White et al., 1999) and N-fixation is not considered a significant N input to terrestrial or aquatic ecosystems in the Emerald Lake watershed (Williams et al., 1995). The impacts of atmospheric deposition on lake trophic status depend on both the

<table>
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<th>Component</th>
<th>Catchment flux</th>
<th>Catchment pool</th>
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</tbody>
</table>

*a Sum of total dissolved P measured in rain and snow, plus wet season (November–April) dry deposition, which accumulates in the snowpack during the winter and is delivered to the lake during snowmelt.

*b Sum of wet and dry-season atmospheric deposition estimates.
total amount of nutrients deposited, and the relative abundances of nutrients present in the deposition. For example, if N deposition greatly exceeds P deposition, then lakes are likely to become P limited. Bytnerowicz et al. (1991) measured the dry deposition of atmospheric total phosphorus in the Emerald Lake watershed and estimated a flux rate during the dry season of 290 μg N m⁻² d⁻¹, which yields a total load of 63 kg N. Using this measure of dry-season N deposition with the P deposition rates arrived at in the present study, yields a molar N/P ratio of 16/1 for dry deposition in the Emerald Lake watershed during the ice-free season. This ratio is much lower than those typically reported in the literature for atmospheric deposition (Markaki et al., 2003; Zhang et al., 2007); however it is similar to values observed at a high-elevation (2900 m) site in Spain (Morales-Baquero et al., 2006), where low N/P ratios were attributed to the relative absence of anthropogenically-enriched aerosols, which tend to have high N/P ratios, and the relatively dry summers, which lead to a dominance of P-enriched dry deposition over N-enriched wet deposition. We propose that the relative input rates of dry N and P estimated for Emerald Lake are consistent with increasing incidence of N limitation of phytoplankton growth and indicate that atmospheric P deposition is a significant cause of long-term eutrophication of Sierra Nevada lakes.

5. Conclusions

Atmospheric deposition of P represents an important nutrient input pathway for oligotrophic aquatic ecosystems and P-poor terrestrial ecosystems (Graham and Duce, 1979; Mahowald et al., 2008). Long-term data from the Sierra Nevada suggest that lakes are experiencing increased P loading; however, there have been very few measurements of atmospheric P concentrations made in the western U.S., and the Sierra Nevada in particular, that can be used to assess whether these trends are being driven by atmospheric processes. We measured TP, IP and OP in coarse and fine atmospheric PM during the dry season in the Sierra Nevada and found that:

1. Atmospheric P dynamics were dominated by IP in the coarse (>1 μm) PM fraction, which was responsible for more than 90% of the estimated depositional flux throughout the study period, consistent with the role of mineral dust as the dominant source of P to the atmosphere.

2. P was particularly enriched in aerosol particles 1.0 – 3.2 μm in diameter, suggesting that long-range aerosol transport may be an important factor determining atmospheric P concentrations at the site. Particles larger than 3.2 μm (local sources), rarely contributed as significantly to atmospheric TP loading.

3. Atmospheric PM derived from intense wildfires in northern and central California was found to be P-enriched in both size fractions; however, a large, but low-intensity local wildfire was not a significant source of particulate P to the atmosphere. We attribute this discrepancy to the differing intensities of the fires and suggest that is a topic of particular interest when considering future research.

4. The relatively high P content and low N:P ratio of dry deposition during the growing season suggests that atmospheric transport is an ecologically significant source of P to high-elevation lakes of the southern Sierra Nevada, and is likely responsible for driving recently observed trophic changes in these lakes.

Acknowledgements

The authors would like to thank the Air Resources Division of Sequoia and Kings Canyon National Park, particularly Annie Esperanza and Heather Veerkamp-Tobin, for their help with experimental design and data collection. Stacked Filter Unit (SFU) components and technical advice regarding ambient particulate matter sampling were graciously provided by Dr. Thomas Cahill and Dr. David Barnes of UC Davis, DELTA Group. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.php) used in this publication. We would also like to thank Delores Lucero and Dr. Kristine Richardson of UC Riverside for their support in the field and help with chemical analysis. This work was funded by the National Science Foundation, Long-Term Research in Environmental Biology program (Award Number 0614207 to J.M. Melack and J.O. Sickman).

References


